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THERMAL ANALYSIS OF SOME ENVIRONMENTALLY DEGRADABLE POLYMERS*

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Abstract

The thermal characteristics of a series of degradable polymers have been investigated using thermogravimetry and differential scanning calorimetry. While the results of the thermogravimetry experiments suggest that the thermal stability of the polymers should not pose any problems at the temperatures that can be expected in a commercial composting process (60°C), phase changes associated with some of the polymers investigated may cause problems in the interpretation of data from composting degradation studies. Several biodegradable polymers were observed to have melt transitions at temperatures similar to those found in a composting environment. Consequently, under the controlled composting conditions used to evaluate biodegradable polymers, degradation of a polymer may be inferred, while actually the polymer has merely undergone a phase change.

Keywords: degradable plastics, polycaprolactone, polyesters, polyethylene, polylactic acid, starch polymers, thermal stability

Introduction

Interest in degradable polymers, once again, is on the rise as entrepreneurs see opportunities in speciality niche markets. It has been forecasted that use of degradable polymers in North America will increase at a rate of 18%/year for the next few years to reach total sales of 0.73 billion kg (1.6 billion lbs) by the year 2000 [1]. The principal markets for these products will be mainly in agricultural mulch film, compost bags, food-service disposables, paper coatings and hygienic products. The possibility of new government regulations in Europe and Japan [2] is seen as the major driver for this expanded usage of degradable polymers, especially the biodegradable variety.

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One of the major rationalizations seen for the increased demand for degradable plastics is the anticipated increase in commercial composting operations to deal with the disposal of the organic fraction of municipal solid waste. Degradable plastics are seen as the ideal answer to deal with the collection of yard and food wastes, as well as dealing with residues from fast food restaurants and institutions, such as hospitals. All these institutions generate high volumes of organic matter that is compostable. In order to ensure that these new polymeric materials are suitable for composting, test procedures are being developed and evaluated to ensure that industrial claims can be validated in terms of actual performance [3]. When the degradability of polymeric materials in a composting environment is considered, the primary degradation mechanism is thought to be biodegradation. Essentially in this process microorganisms, such as bacteria and fungi, degrade the material producing CO_2 and other natural products. However, because of the elevated temperatures associated with commercial composting operations (i.e. 60–65°C) coupled with the presence of moisture, and oxygen, other chemical degradation processes can occur. Consequently materials can be designed to use these conditions to promote reactions which may lead to the breakdown of the polymeric material producing material of a reduced molecular weight as a result of degradation. This approach has been used with polymers such as polyethylene, to which catalysts, usually transition metal compounds used in combination with peroxides, have been added to the polymer to promote oxidative degradation [4, 5]. Consequently when examining the behaviour of polymeric materials for their suitability as compost bags one has to ask several questions. What is the purpose of the plastic material and what are the degradation products produced in the composting environment? Depending upon the answers to these questions biodegradation may not be the key requirement. A hydrolyticaly degradable or thermally oxidative degradable polymer may be just as acceptable. It is also possible that the use of a polymer with a thermal phase change at temperatures encountered in a composting operation may be sufficient to achieve the desired results.

In an earlier study, we reported on the role of different environmental exposures on the degradation of a range of degradable polymeric materials [6]. This earlier study involved the exposure of a variety of degradable polymeric materials to: laboratory-scale composting, thermohydrolytic exposure at 60°C and dry thermal oxidation also at 60°C. The results of the study indicated that while both chemical and biological degradation were occurring with many of the polymers investigated, several of the polymers also underwent physical transitions and restructuring at temperatures encountered in a typical commercial composting operation. These changes were identified as being responsible for some of the physical changes noted during composting. It was therefore decided to use thermal analysis to investigate the thermal properties of several of the polymeric materials currently being proposed as polymeric materials for use in commercial composting facilities.

Experimental

Materials

The test samples evaluated in this study are described in Table 1. These polymeric materials represent most of the degradable polymers that are currently commercially available and have been promoted for their applicability to composting operations. They include starch based polymers blended with other polymers; polymers based upon polycaprolactone and polylactic acid as well as several polyethylene based polymers containing additive packages. The sources of these materials along with their chemical composition are also listed in Table 1.

Thermal analysis

The thermal properties of the materials were determined using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) using a TA Instruments 2100 Thermal Analyser. The TG module used was a Model 951, while the DSC module was a Model 910.

The TG experiments were conducted in helium, controlled at a flow rate of 50 mL min^{-1}. Sample sizes were approximately 10 mg and the experiments were conducted at a heating rate of 10°C min^{-1} from room temperature up to 900°C.

The DSC experiments were performed on samples weighing approximately 5 mg. These samples were weighed into standard aluminum pans and sealed. The samples were then placed in the DSC unit and cooled to 150°C. The samples were then heated at 10°C min^{-1} to 200°C in nitrogen at a flow rate of 50 mL min^{-1}. On completion of the first heating scan the samples were slowly cooled with liquid nitrogen and a second heating scan performed on the same sample.

Results and discussion

Thermal stability as measured by TG

Thermogravimetry has long been used as a measure of the thermal stability of polymeric materials. Frequently, simple TG experiments are performed to determine the degradation temperature of a particular polymeric material, reporting such values as onset temperature and peak degradation temperature, etc. Unfortunately these properties are not absolute values typical of a polymeric material but are greatly dependent upon many factors such as sample size, heating rate, test environment, etc. Consequently any such values reported in the literature have to be interpreted with caution. In the same way, the values reported in this study are specific to the experimental conditions used. In addition it should be noted that mass loss alone should not be used to predict the stability or 'lifetime' of a particular polymer [7]. Many systems can undergo irreversible loss in physical properties while minimal mass loss occurs.

Table 1 Commercially degradable polymers examined in this study

Code	Sample name	Composition	Supplier	Application	Thickness/ μm
B1	Biopol	Poly(hydroxy butyrate valerate)	ICI	mulch film	
T1	Tone	Polycaprolactone P-787	Union Carbide (USA)	compost bag	26
MB1	Mater-Bi ZF03U	Polycaprolactone/starch/synthetic blend	Novamont (Italy)	compost bag	54
MB2	Mater-Bi Z101U/T	Polycaprolactone/starch/synthetic blend		sheet	103
EP	Eco-Pla	Polylactic acid	Cargill (USA)	film	48
N1	Novon	Destructurized/gelatinized starch based polymer	Farnell Canada	compost bag	46
ES1	Naturegrade+	77% LLDPE+23% Master batch	Ecostar^{+} (USA)	compost bag	46
BS1	Bio-Solo Brown	Polyethylene+additive package	Indaco (Canada)	compost bag	32
BS2	Bio-Solo Green	Polyethylene+additive package	Indaco (Canada)	compost bag	37
EV1	Enviro White	Polyethylene+additive package	EPI (USA)	compost bag	40
EV2	Enviro Green	Polyethylene+additive package	EPI (USA)	film	29
EV3	Enviro Black	Polyethylene+additive package	EPI (USA)	garbage bag	32
C1	Control	Standard black garbage bag	B&G (Canada)	garbage bag	26

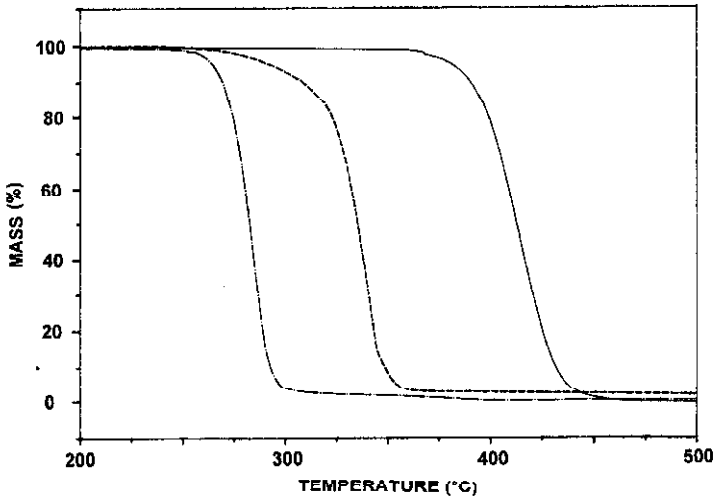

Fig. 1 TG curves for Tone (—), Eco-Pla (- - -) and Biopol (– · –) polymers heated at 10°C min^{-1} in helium

The mass loss behaviour of the Biopol (B1); Tone, polycaprolactone polymer (T1) and the Eco Pla, polylactic acid polymer (EP) are presented in Fig. 1. From this figure it can be seen that the Tone polycaprolactone (T1) is much more thermally stable than the Eco Pla, polylactic acid (EP) which itself is more thermally stable than the Biopol (B1) polymer. The onset of degradation temperature, major degradation range and peak degradation temperature are all summarized in Table 2. Based upon these mass loss curves it would appear that all of these polymers are relatively stable up to temperatures of about 250°C. Above 250°C. however. the Biopol polymer (B1) starts to lose weight rapidly and has a peak degradation temperature below 300°C, at 286.7°C. The polylactic acid polymer (EP), meanwhile, does not show any rapid lose in weight until about 317–351°C. Although the onset and degradation temperature ranges noted with the polylactic acid in this study are similar to those reported by Kopinke [8], they observed two well-resolved degradation steps when heated at 5°C min^{-1}, while only one degradation stage is evident in Fig. 1. The Tone polymer (T1), meanwhile, appears to have a higher thermal stability. The mass loss curve for this polymer shows little change below 360°C. However, rapid mass loss is noted between 383–444°C with the polymer producing no residue.

The thermal mass loss behaviour of the two Mater-Bi samples is presented in Fig. 2. It will be noted that while both samples showed similar mass loss characteristics, (i.e. two stage degradation processes centred around 320 and 400°C), both polymers also displayed some mass loss behaviour below 275°C, which appeared typical of starch containing materials. Both samples were also observed to have measurable residues at 700°C.

The mass loss curves for the Novon (N1) and Naturegrade$^+$ polymers are presented in Fig. 3. The starch based Novon (N1) displayed many similar characteristics to those noted with the two other starch containing polymers MB1 and MB2. The polymer displayed signs of mass loss below 200°C. It also lost weight

Table 2 TG data (10°C min^{-1} heating rate)

Code	Sample name	Onset/ °C	Major degradation range/°C	Peak temp./ °C	Residue @ 700°C/%
B1	Biopol	243.7	263–298	286.7	0.0
T1	Tone	363.3	383–444	413.6	0.0
MB1	Mater-Bi ZF03U	123.8	355–429	391.5	5.13
MB2	Mater-Bi Z101U/T	56.1	374–440	410.8	11.3
EP	Eco-Pla	253.6	317–357	339.5	0.79
N1	Novon	101.6	364–419	390.1	0.49
ES1	Naturegrade$^+$	239.4	448–500	480.6	3.54
BS1	Bio-Solo Brown	420.3	441–493	474.1	16.0
BS2	Bio-Solo Green	400.1	440–494	474.3	14.6
EV1	Enviro White	399.5	440–491	469.2	4.7
EV2	Enviro Green	413.2	444–496	477.5	2.4
EV3	Enviro Black	408.6	443–498	476.5	35.8
C1	Control	410.9	447–499	479.2	3.0

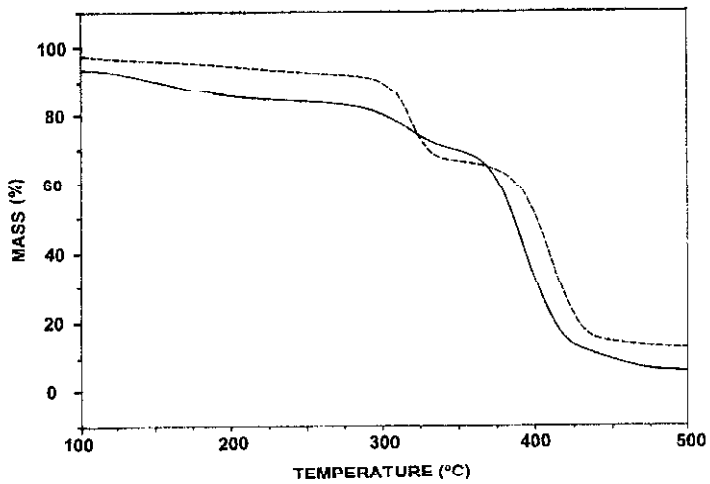

Fig. 2 TG curves for Mater-Bi ZFO3U (—) and Mater-Bi Z101U/T (- - -) polymers heated at 10°C min^{-1} in helium

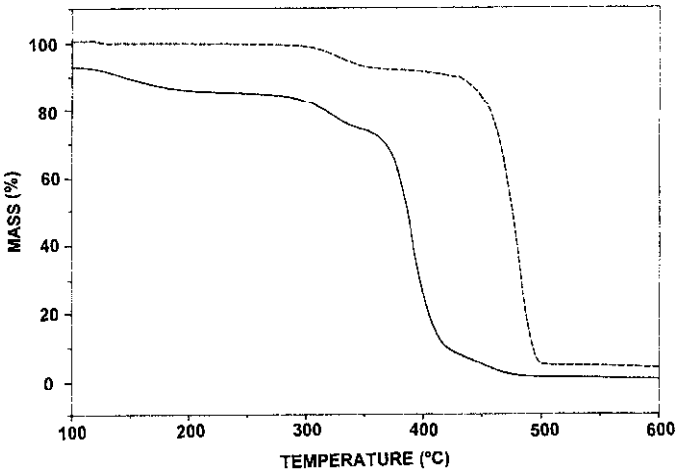

Fig. 3 TG curves for Novon (—) and Naturegrade$^+$ (- - -) polymers heated at 10°C min^{-1} in helium

in two stages centred around 320 and 390°C values similar to those observed with MB1. Like the MB1 sample, the Novon material also demonstrated a slow but gradual loss in weight between 400 and 480°C. The Naturegrade$^+$ (ES1) sample meanwhile, demonstrated a mass loss behaviour similar to polyethylene. For example the principal mass loss occurred in the temperature range 450–500°C with a peak degradation temperature of 480.0°C (polyethylene shown in Fig. 4 has a peak temperature of 479.2°C). However, the sample also showed some mass loss centred around 330°C. Although the actual mass loss in this region was only 7.8%, the data appears to confirm the presence of starch in the polymer.

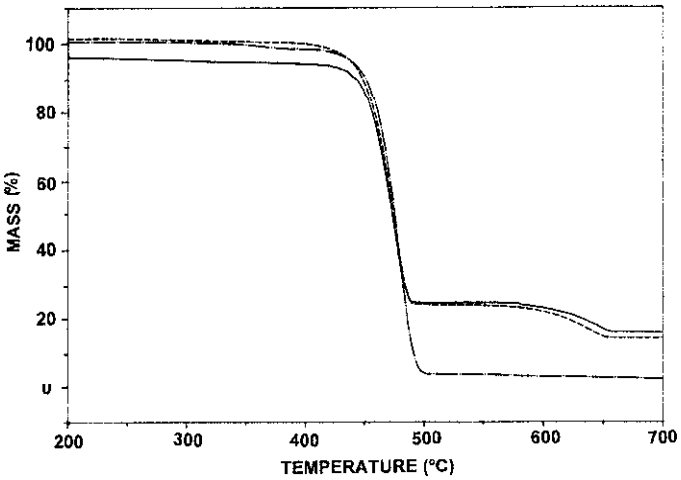

Fig. 4 TG curves for Bio-solo Brown (—), Bio-solo Green (- - -) and LLDPE control (– · –) polymers heated at 10°C min^{-1} in helium

Figure 4 presents the mass loss data for the two polymers BS1 and BS2. These two polymers are polyethylene based and contain additive packages. Also presented in this figure is data obtained with a standard black polyethylene garbage bag that was run as a control (C1). It will be noted that all three samples gave similar mass loss curves with the onset of degradation occurring around 410°C and the principal mass loss taking place between 440 and 500°C. However, some slight differences were noted in the case of the Bio-Solo polymers. For example the peak degradation temperatures were slightly lower 474.1°C (BS1) and 474.3°C (BS2) than those reported for the control of 479.2°C. In addition both Bio-Solo polymers exhibited slow mass loss processes between 500 and 650°C which accounted for an additional 10% mass loss and both samples also had relatively high residual solids.

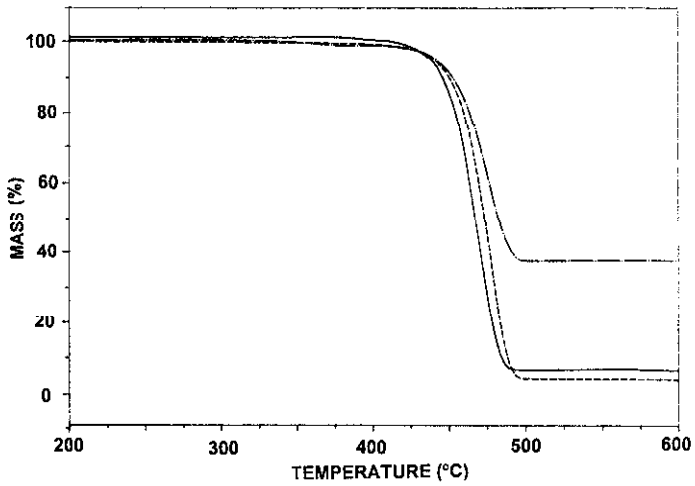

Fig. 5 TG curves for Enviro White (—), Enviro Green (- - -) and Enviro Black (– · –) polymers heated at 10°C min^{-1} in helium

The mass loss behaviour of the three other polyethylene based polymers Enviro White (EV1), Enviro Green (EV2) and Enviro Black (EV3) are presented in Fig. 5. The mass loss behaviour of these three polymers once again reflect those observed with the polyethylene control. For example their onset temperatures occur close to 410°C with the major degradation occurring between 440 and 500°C. Once again the peak degradation temperatures were slightly lower than those reported for the control (C1), but unlike the Bio-Solo polymers no extended degradation was observed in the 500–650°C region. The Enviro Black (EV3) sample was noted to have an exceptionally high residue in comparison to other film samples examined.

DSC measurements

While TG is capable of measuring polymer stability in terms of mass loss it fails to indicate any structural or physical changes taking place within the polymer system which can influence the morphology, and consequently the physical properties. With many polymeric systems two solid states can be distinguished, the crystalline state and the glassy state, with the transition from the glassy state to the rubber state being classified as the glass transition temperature. This temperature is important in determining the behaviour of the polymeric material especially as it relates to the physical properties and its anticipated performance in a changing temperature environment, such as that found in a typical composting operation. However it should be noted that in the case of starch based polymers, water can have a profound effect upon the measured thermal properties, due to its plasticizing effect [9]. Consequently, while the DSC gives information on the thermal behaviour of the polymer in a dry inert atmosphere, its behaviour in a composting environment in which moisture, air and biological agents are present could be difficult.

The DSC scans for the Biopol (B1), the Tone (T1) and the Eco-Pla polymers (EP) are presented together in Fig. 6. In the case of the Tone polymer (T1) the T_g is only just discernible at about –64.3°C. The melting transition at 55.1°C is however sharp and only one peak is discernable. The measured heat of fusion of 40.2 J g^{-1} suggests a crystallinity of 53% based on a value of 76.5 J g^{-1} for 100% crystalline polycaprolactone reported by Huang [10]. In the case of Eco-Pla (EP) no melting transition was detected prior to the onset of degradation at about 300°C. Although other researchers have reported melting peaks between 171 and

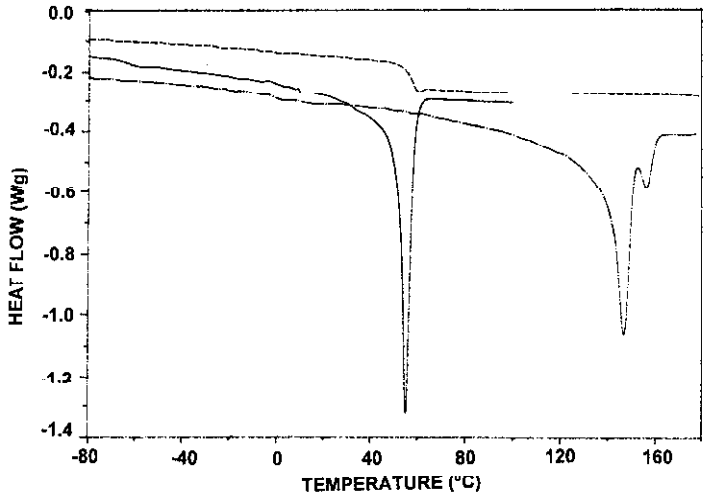

Fig. 6 DSC curves for Tone (—), Eco-Pla (- - -) and Biopol (– · –) polymers heated at 10°C min^{-1} in nitrogen

178°C [9, 11], a single T_g at 56.7°C was the only thermal transition noted between −100 and 300°C in all DSC scans.

In the case of the Biopol polymer (B1), a glass transition temperature of about −5.9°C is detected along with a double peaked melting transition located at 146.9 and 156.3°C. This measured glass transition temperature for Biopol is a little low compared to values reported for the commercial polymer of about 5°C [12]. However, the butyl to valerate ratio is known to influence both the T_g as well as the melting point [13–16] with both the T_g and melt temperature decreasing as the amount of valerate in the material increases. This also helps to explain the lower melting temperature and enthalpies presented in Table 3 when compared to literature values of T_m=177–178°C and ΔH_f=85.5 g^{-1} reported for the pure poly hydroxy butyrate [17]. Using literature values for the heats of fusion of mixed PHB and PHV systems (e.g. ΔH_f=25 J g^{-1} for 45% PHB and 7 J g^{-1} for 7% PHB) [14] suggest that the interpolated PHB content of the Biopol used in this study was 80%.

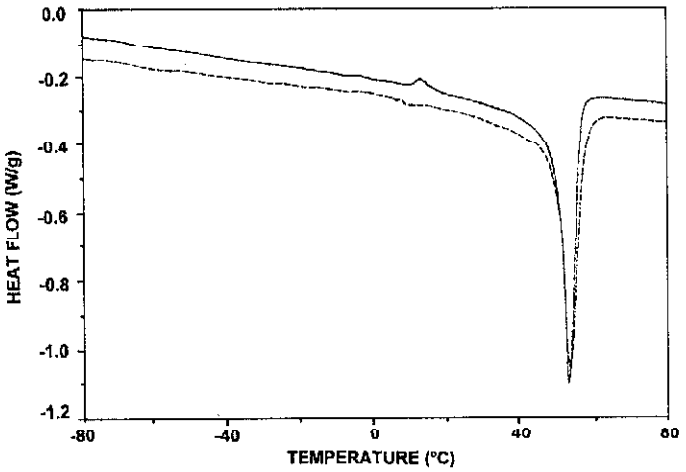

Fig. 7 DSC curves for Mater-Bi ZF03U (—) and Mater-Bi Z101U/T (- - -) polymers heated at 10°C min^{-1} in nitrogen

The DSC results obtained with the starch-based Mater-Bi samples are presented in Fig. 7 and summarised in Table 3. Because Mater-Bi samples are available in several grades which differ by structure and composition some variability in reported thermal properties is to be expected. However, the two samples studied in this investigation had very similar T_g's (−66.4 and −65.3°C) and heats of fusion.

The Novon sample (N1) like the Mater-Bi samples is based upon modified starch and starch blend technology. The DSC behaviour of this polymer is shown in Fig. 8 and summarised in Table 3. Clearly the results correlate with those ob-

tained with the two Mater-Bi samples (i.e. a T_g at –67.1°C and a melting temperature of 54.6°C). The measured heat of fusion, of 34.8 J g^{-1}, is however slightly higher than that noted with the Mater-Bi samples (MB1, MB2).

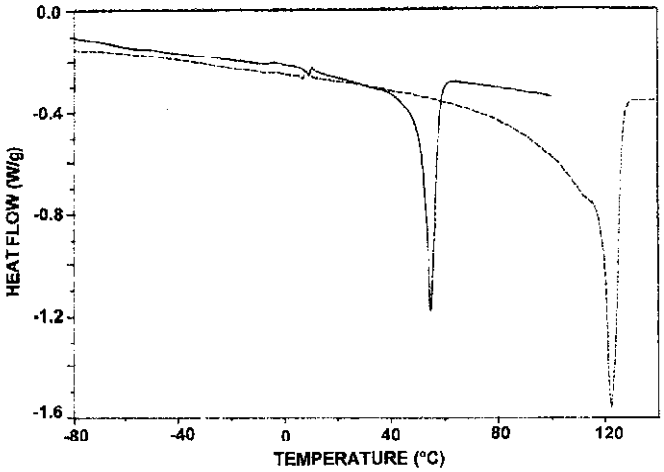

Fig. 8 DSC curves for Novon (—) and Naturegrade$^+$ (- - -) polymers heated at 10°C min^{-1} in nitrogen

Table 3 DSC data (10°C min^{-1} heating rate)

Code	Sample name	T_g/°C	T_m/°C	ΔH_f/J g^{-1}
B1	Biopol	–5.9	146.9	55.7
T1	Tone	–64.3	55.1	40.2
MB1	Mater-Bi ZF03U	–66.4	52.9	27.7
MB2	Mater-Bi Z101U/T	–65.3	53.3	26.9
EP	Eco-Pla	56.7	–	–
N1	Novon	–67.1	54.6	34.8
ES1	Naturegrade$^+$	–41.1	122.0	95.0
BS1	Bio-Solo Brown	–20.5	122.2	80.5
BS2	Bio-Solo Green	–22.7	122.5	79.0
EV1	Enviro White	–27.2	109.4	92.8
EV2	Enviro Green	–38.4	123.7	89.0
EV3	Enviro Black	–26.0	105.3	86.5
C1	Control	–22.2	121.6	95.1

The Naturegrade polymer which consists of polyethylene compounded with an Ecostar package, shows the characteristic melting typical of polyethylene i.e.

a peak centred at 122°C in addition to a shoulder at about 110°C. Although some differences were noted in the shape of the melting peak of the Naturegrade sample (ES1) when compared with the LLDPE control (C1) (Fig. 9) the measured peak temperatures and heats of fusion are similar. The observed enthalpy corresponds to 32% crystallinity using a value of 291.3 J g^{-1} for the enthalpy of fusion for 100% crystalline polyethylene [16]. The DSC traces of the Bio-Solo samples are presented in Fig. 9 along with that of the standard LLDPE control, obtained from a commercial garbage bag. It will be noted that both these Bio-Solo samples have multi-melting peaks similar to that noted for the control. However, some changes are noted, suggesting different thermal histories. In addition the measured heats of fusion for the degradable polymers are substantially less than those measured for the control.

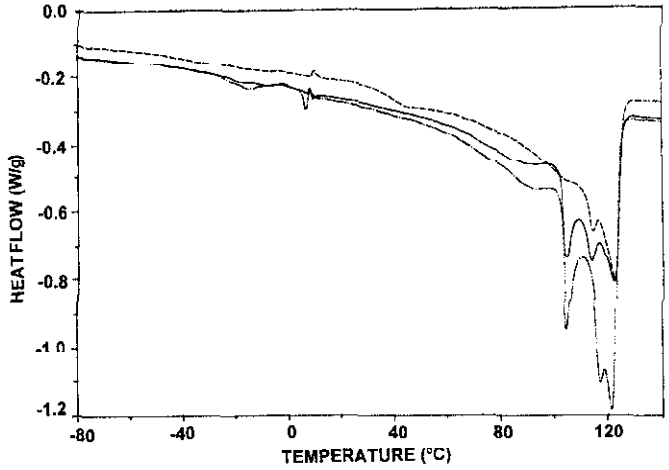

Fig. 9 DSC curves for Bio-solo Brown (—), Bio-solo Green (- - -) and LLDPE control (– · –) polymers heated at 10°C min^{-1} in nitrogen

In the case of the three Enviro samples EV1, EV2 and EV3, only the EV2 sample appears to have the multiple melting point peaks noticed with the LLDPE control C1. However, even this sample has some differences, suggesting differences in thermal processing history. Meanwhile the EV1 and EV3 samples were noted to have lower melting temperatures (i.e. 109.4 and 105.3°C, respectively) than the LLDPE control (121.6°C). In addition both these samples displayed a lack of multiple melting endotherms, observed with the other polyethylene samples. The importance of these multiple melting endotherms, which have been attributed to morphological features associated with the crystalline lamellar, remains unsure when addressing the compostability of the materials. However, the fact that they occur at temperatures substantially higher than those encountered in commercial composting operations would suggest that they would have little, if any effect.

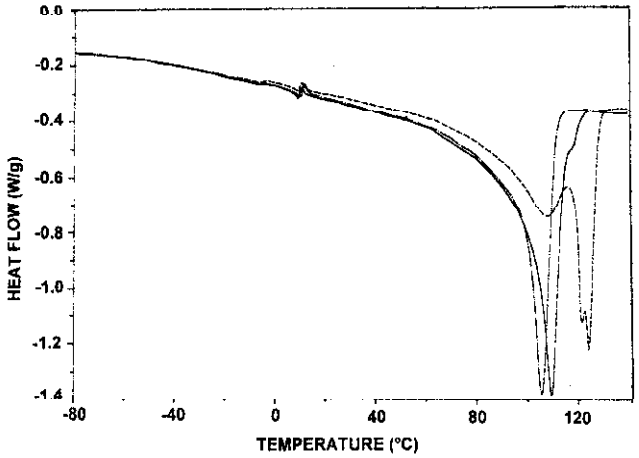

Fig. 10 DSC curves for Enviro White (—), Enviro Green (- - -) and Enviro Black (– · –) polymers heated at 10°C min^{-1} in nitrogen

Conclusions

Based upon the results of this study it is clear that several degradable polymers can undergo phase transitions in the temperature range encountered in a commercial composting operation (20–70°C). Consequently when assessing the biodegradability of a specific polymeric system in such an environment, it is essential to ensure that the observed loss in physical or mechanical properties is due to degradation processes and not due to phase changes only. For example, because of their low melting temperatures it is possible for the Tone (T1), Novon (N1) and the two Mater-Bi (MB1 and MB2) samples to actually melt in a composting environment. Thus films of these materials may disappear without the polymer actually degrading. On the other hand these phase changes could make the material more amenable to subsequent biological degradation in the compost environment.

With a glass transition temperature of 56.7°C the polylactic acid polymer (EP) could also undergo morphological changes during the composting process as the compost heats up and subsequently cools down. Although these changes may not be as dramatic, they could lead to morphological changes, which could influence subsequent physical properties.

In the case of the other polymers investigated, no thermally induced process seems to be occurring at the temperatures typically found in a composting system. Consequently any changes noted with these polymers in a composting process can be attributed to degradation processes.

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